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**ASCORBIC ACID COMPOUNDS AS REDUCING AGENTS FOR
THERMALLY DEVELOPABLE COMPOSITIONS AND IMAGING
MATERIALS**

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**ASCORBIC ACID COMPOUNDS AS REDUCING AGENTS FOR
THERMALLY DEVELOPABLE COMPOSITIONS
AND IMAGING MATERIALS**

5 FIELD OF THE INVENTION

This invention relates to thermally developable compositions and imaging materials (both thermographic and photothermographic materials) comprising certain ascorbic acid compounds as the reducing agents for the non-photosensitive source of silver ions. Imaging materials containing these
10 compounds have improved post-processing stability.

BACKGROUND OF THE INVENTION

Silver-containing photothermographic imaging materials (that is, thermally developable photosensitive imaging materials) that are imaged with
15 actinic radiation and then developed using heat and without liquid processing have been known in the art for many years. Such materials are used in a recording process wherein an image is formed by imagewise exposure of the photothermographic material to specific electromagnetic radiation (for example, X-radiation, or ultraviolet, visible, or infrared radiation) and developed by the use of thermal
20 energy. These materials, also known as "dry silver" materials, generally comprise a support having coated thereon: (a) a photocatalyst (that is, a photosensitive compound such as silver halide) that upon such exposure provides a latent image in exposed grains that are capable of acting as a catalyst for the subsequent formation of a silver image in a development step, (b) a relatively or completely
25 non-photosensitive source of reducible silver ions, (c) a reducing composition (usually including a developer) for the reducible silver ions, and (d) a hydrophilic or hydrophobic binder. The latent image is then developed by application of thermal energy.

In photothermographic materials, exposure of the photographic
30 silver halide to light produces small clusters containing silver atoms (Ag^0)_n. The imagewise distribution of these clusters, known in the art as a latent image, is generally not visible by ordinary means. Thus, the photosensitive material must

be further developed to produce a visible image. This is accomplished by the reduction of silver ions that are in catalytic proximity to silver halide grains bearing the silver-containing clusters of the latent image. This produces a black-and-white image. The non-photosensitive silver source is catalytically reduced to
5 form the visible black-and-white negative image while much of the silver halide, generally, remains as silver halide and is not reduced.

In photothermographic materials, the reducing agent for the reducible silver ions, often referred to as a “developer,” may be any compound that, in the presence of the latent image, can reduce silver ion to metallic silver
10 and is preferably of relatively low activity until it is heated to a temperature sufficient to cause the reaction. A wide variety of classes of compounds have been disclosed in the literature that function as developers for photothermographic materials. At elevated temperatures, the reducible silver ions are reduced by the reducing agent. In photothermographic materials, upon heating, this reaction
15 occurs preferentially in the regions surrounding the latent image. This reaction produces a negative image of metallic silver having a color that ranges from yellow to deep black depending upon the presence of toning agents and other components in the imaging layer(s).

20 **Differences Between Photothermography and Photography**

The imaging arts have long recognized that the field of photothermography is clearly distinct from that of photography. Photothermographic materials differ significantly from conventional silver halide photographic materials that require processing with aqueous processing solutions.

25 In photothermographic imaging materials, a visible image is created by heat as a result of the reaction of a developer incorporated within the material. Heating at 50°C or more is essential for this dry development. In contrast, conventional photographic imaging materials require processing in aqueous processing baths at more moderate temperatures (from 30°C to 50°C) to
30 provide a visible image.

In photothermographic materials, only a small amount of silver halide is used to capture light and a non-photosensitive source of reducible silver ions (for example a silver carboxylate or a silver benzotriazole) is used to generate the visible image using thermal development. Thus, the imaged photosensitive silver halide serves as a catalyst for the physical development process involving the non-photosensitive source of reducible silver ions and the incorporated reducing agent. In contrast, conventional wet-processed, black-and-white photographic materials use only one form of silver (that is, silver halide) that, upon chemical development, is itself at least partially converted into the silver image, or that upon physical development requires addition of an external silver source (or other reducible metal ions that form black images upon reduction to the corresponding metal). Thus, photothermographic materials require an amount of silver halide per unit area that is only a fraction of that used in conventional wet-processed photographic materials.

In photothermographic materials, all of the "chemistry" for imaging is incorporated within the material itself. For example, such materials include a developer (that is, a reducing agent for the reducible silver ions) while conventional photographic materials usually do not. Even in so-called "instant photography," the developer chemistry is physically separated from the photosensitive silver halide until development is desired. The incorporation of the developer into photothermographic materials can lead to increased formation of various types of "fog" or other undesirable sensitometric side effects. Therefore, much effort has gone into the preparation and manufacture of photothermographic materials to minimize these problems.

Moreover, in photothermographic materials, the unexposed silver halide generally remains intact after development and the material must be stabilized against further imaging and development. In contrast, silver halide is removed from conventional photographic materials after solution development to prevent further imaging (that is in the aqueous fixing step).

Because photothermographic materials require dry thermal processing, they present distinctly different problems and require different

materials in manufacture and use, compared to conventional, wet-processed silver halide photographic materials. Additives that have one effect in conventional silver halide photographic materials may behave quite differently when incorporated in photothermographic materials where the chemistry is significantly more complex. The incorporation of such additives as, for example, stabilizers, antifoggants, speed enhancers, supersensitizers, and spectral and chemical sensitizers in conventional photographic materials is not predictive of whether such additives will prove beneficial or detrimental in photothermographic materials. For example, it is not uncommon for a photographic antifoggant useful in conventional photographic materials to cause various types of fog when incorporated into photothermographic materials, or for supersensitizers that are effective in photographic materials to be inactive in photothermographic materials.

These and other distinctions between photothermographic and photographic materials are described in *Imaging Processes and Materials* (Neblette's Eighth Edition), noted above, *Unconventional Imaging Processes*, E. Brinckman et al. (Eds.), The Focal Press, London and New York, 1978, pp. 74-75, in Zou et al., *J. Imaging Sci. Technol.* **1996**, *40*, pp. 94-103, and in M. R. V. Sahyun, *J. Imaging Sci. Technol.* **1998**, *42*, 23.

Problem to be Solved

Photothermographic materials have not achieved wide use in X-radiography because they have generally had relatively low photographic speed or exhibited haze associated with the various conventional imaging components.

Photothermographic materials have been described in the art to include various non-photosensitive sources of reducible silver ions including silver salts of benzotriazole and silver salts of its derivatives [see for example, U.S. Patent 6,576,410 (Zou et al)].

The reduction of the silver ions in silver benzotriazole to silver metal in photothermographic materials generally requires a relatively strong reducing agent. A typical developer choice is ascorbic acid that has been shown to

provide useful photospeed, adequate D_{max}, and low D_{min}. Derivatives (such as esters) of ascorbic acid have also been described as reducing agents for silver ions in organic silver salts. For example, ascorbic acid palmitate and dipalmitate are described for this purpose in U.S. Patents 4,543,309 (Hirabayashi et al.) and
5 4,451,561 (Hirabayashi et al.) and ascorbic acid stearate, myristate, and laurate are described for this purpose in U.S. Patents 3,832,186 (Masuda et al.) and 3,881,938 (Masuda et al.) and FR 1,542,505 (Okubo et al.).

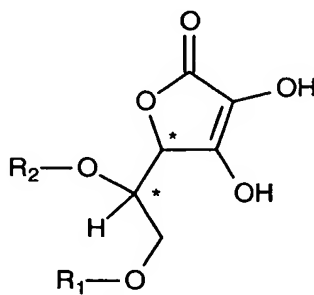
There is continuing work in the art to develop thermally developable materials using silver benzotriazole and other organic silver salts that
10 require relatively strong reducing agents. Because some imaging systems include components that may lead to image instability, especially in aqueous-based imaging materials, there is a continuing need to find the most suitable silver ion reducing agents in order to obtain optimal sensitometric properties and to improve post-processing light stability of the imaged materials.

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SUMMARY OF THE INVENTION

The present invention provides a thermally-developable composition comprising a binder, and in reactive association, a non-photosensitive source of reducible silver ions that includes a compound containing an imino
20 group, and a reducing agent for the non-photosensitive source of reducible silver ions,

the reducing agent being a compound, or mixture thereof, represented by the following Structure (I):



(I)

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wherein R_1 and R_2 are independently hydrogen or an acyl group having 11 or fewer carbon atoms, provided that at least one of R_1 and R_2 is an acyl group.

This invention also provides a black-and-white photothermo-
5 graphic material comprising a support and having on at least one side thereon one or more thermally developable imaging layers comprising a binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, a reducing agent for the non-photosensitive reducible silver ions, and
10 optionally an outermost protective layer disposed over the one or more thermally developable imaging layers,

wherein the reducing agent is a compound, or mixture thereof, represented by the Structure (I) noted above.

In preferred embodiments of this invention, a black-and-white
15 aqueous-based photothermographic material comprises a transparent support having on at least one side thereof:

a) one or more thermally developable imaging layers each comprising a hydrophilic binder that is gelatin, a gelatin derivative, a poly(vinyl alcohol), or a cellulosic material, or is a water-dispersible polymeric latex, and in reactive
20 association,

a preformed photosensitive silver bromide, silver iodobromide, or a mixture thereof, provided predominantly as tabular grains,

a non-photosensitive source of reducible silver ions that includes one or more organic silver salts at least one of which is predominantly a silver salt
25 of benzotriazole,

a reducing agent for the non-photosensitive source of reducible silver ions, and

b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers, and

30 wherein the reducing agent is selected from the list of compounds in TABLE I noted below, or is a mixture thereof.

In additional preferred embodiments, a black-and-white photo-thermographic material comprises a support having on a frontside thereof,

5 a) one or more frontside thermally developable imaging layers comprising a hydrophilic polymer binder or water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photo-sensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, a reducing agent for the non-photosensitive source reducible silver ions, and

10 the material comprising on the backside of the support, one or more backside thermally developable imaging layers comprising a hydrophilic polymer binder or a water-dispersible polymer latex binder, and in reactive association, a photosensitive silver halide, a non-photosensitive source of reducible silver ions that includes a silver salt of a compound containing an imino group, and a

15 b) optionally, an outermost protective layer disposed over the one or more thermally developable imaging layers on either or both sides of the support, and

20 wherein the one or more thermally developable imaging layers, or the one or more protective layers if present, on both sides of the support have the same or different composition, and

 the reducing agents on both sides of the support are the same or different and each reducing agent is a compound, or mixture thereof, represented by the Structure (I) noted above.

25 This invention also provides a method of forming a visible image comprising:

 A) imagewise exposing the photothermographic material of this invention to form a latent image,

 B) simultaneously or sequentially, heating the exposed photothermographic material to develop the latent image into a visible image.

Where the noted method is carried out using a thermally developable material comprising a transparent support, the image-forming method can further comprise:

5 C) positioning the exposed and thermally-developed material with the visible image therein between a source of imaging radiation and an imageable material that is sensitive to the imaging radiation, and

D) exposing the imageable material to the imaging radiation through the visible image in the exposed and thermally-developed material to provide an image in the imageable material.

10 Thermographic materials of this invention can be similarly used to provide an image, but the latent image is formed using thermal energy and development occurs simultaneously with imaging.

The images formed in both thermographic and photothermographic materials of this invention can be used for medical diagnosis.

15 An imaging assembly of the present invention comprises a photothermographic material of the present invention that is arranged in association with one or more phosphor intensifying screens. A method of forming a black-and-white image can then comprise exposing the imaging assembly to X-radiation.

20 We have discovered that the specific ascorbic acid derivatives described herein by Structure I provide improved post-processing stability of images obtained in thermally developable materials that include reducible silver ions in silver salts that contain an imino group, such as silver benzotriazole.

25 **DETAILED DESCRIPTION OF THE INVENTION**

The thermally developable materials of this invention can be used in black-and-white or color photothermography and in electronically generated black-and-white or color hardcopy recording. They can be used in microfilm applications, in radiographic imaging (for example digital medical imaging),
30 X-ray radiography, and in industrial radiography. Furthermore, the absorbance of these materials between 350 and 450 nm is desirably low (less than 0.5), to permit

their use in the graphic arts area (for example, imagesetting and phototypesetting), in the manufacture of printing plates, in contact printing, in duplicating ("duping"), and in proofing.

5 The photothermographic materials of this invention are particularly useful for medical imaging of human or animal subjects in response to visible or X-radiation for use in medical diagnosis. Such applications include, but are not limited to, thoracic imaging, mammography, dental imaging, orthopedic imaging, general medical radiography, therapeutic radiography, veterinary radiography, and auto-radiography. Increased sensitivity to X-radiation can be imparted through the use of phosphors. When used with X-radiation, the photothermographic materials of this invention may be used in combination with one or more phosphor intensifying screens, with phosphors incorporated within the photothermographic emulsion, or with a combination thereof.

15 The photothermographic materials of this invention can be made sensitive to radiation of any suitable wavelength. Thus, in some embodiments, the materials are sensitive at ultraviolet, visible, near infrared, or infrared wavelengths of the electromagnetic spectrum. In these embodiments, the materials are preferably sensitive to radiation greater than 350 nm (such as sensitivity to, from about 350 nm to about 450 nm). Increased sensitivity to a particular region of the spectrum is imparted through the use of various sensitizing dyes.

20 The photothermographic materials of this invention are also useful for non-medical uses of visible or X-radiation (such as X-ray lithography and industrial radiography). In these and other imaging applications, it is particularly desirable that the photothermographic materials be "double-sided."

25 In some embodiments of the thermally developable materials of this invention, the components needed for imaging can be in one or more imaging or emulsion layers on one side ("frontside") of the support. The layer(s) that contain the photosensitive photocatalyst (such as a photosensitive silver halide) for photothermographic materials or the non-photosensitive source of reducible silver ions, or both, are referred to herein as the emulsion layer(s). In photothermographic materials, the photocatalyst and non-photosensitive source of

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reducible silver ions are in catalytic proximity and preferably are in the same emulsion layer. Various non-imaging layers can also be disposed on the “backside” (non-emulsion or non-imaging side) of the materials, including, conductive layers, antihalation layer(s), protective layers, antistatic layers, and transport enabling layers.

Various non-imaging layers can also be disposed on the “frontside” or imaging or emulsion side of the support, including protective topcoat layers, primer layers, interlayers, opacifying layers, antistatic layers, antihalation layers, acutance layers, auxiliary layers, and other layers readily apparent to one skilled in the art.

For some embodiments it may be useful that the thermally developable materials be “double-sided” or “duplitized” and have the same or different emulsion coatings (or imaging layers) on both sides of the support. In such constructions each side can also include one or more protective topcoat layers, primer layers, interlayers, antistatic layers, acutance layers, antihalation layers, auxiliary layers, conductive layers, anti-crossover layers, and other layers readily apparent to one skilled in the art.

When the photothermographic materials of this invention are heat-developed as described below in a substantially water-free condition after, or simultaneously with, imagewise exposure, a silver image (preferably a black-and-white silver image) is obtained.

Definitions

As used herein:

In the descriptions of the thermally developable materials of the present invention, “a” or “an” component refers to “at least one” of that component [for example, the ascorbic acid derivatives of Structure (I)].

Heating in a substantially water-free condition as used herein, means heating at a temperature of from about 50°C to about 250°C with little more than ambient water vapor present. The term “substantially water-free condition” means that the reaction system is approximately in equilibrium with

water in the air and water for inducing or promoting the reaction is not particularly or positively supplied from the exterior to the material. Such a condition is described in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman Kodak Company, Rochester, NY, 1977, p. 374.

5 “Photothermographic material(s)” means a construction comprising at least one photothermographic emulsion layer or a photothermographic set of emulsion layers (wherein the photosensitive silver halide and the source of reducible silver ions are in one layer and the other essential components or desirable additives are distributed, as desired, in the same layer or in an adjacent
10 coated layer. These materials also include multilayer constructions in which one or more imaging components are in different layers, but are in “reactive association.” For example, one layer can include the non-photosensitive source of reducible silver ions and another layer can include the reducing agent and/or photosensitive silver halide.

15 “Thermographic material(s)” can be similarly constructed but are intentionally non-photosensitive (thus no photosensitive silver halide is intentionally added).

 When used in photothermography, the term, “imagewise exposing” or “imagewise exposure” means that the material is imaged using any exposure
20 means that provides a latent image using electromagnetic radiation. This includes, for example, by analog exposure where an image is formed by projection onto the photosensitive material as well as by digital exposure where the image is formed one pixel at a time such as by modulation of scanning laser radiation.

 When used in thermography, the term “imagewise exposing” or
25 “imagewise exposure” means that the material is imaged using any suitable thermal energy imaging source such as a thermal print head.

 “Catalytic proximity” or “reactive association” means that the materials are in the same layer or in adjacent layers so that they readily come into contact with each other during thermal imaging and development.

30 “Emulsion layer,” “imaging layer,” or “photothermographic (or “thermographic”) emulsion layer,” means a layer of a photothermographic (or

thermographic) material that contains the photosensitive silver halide (not present in thermographic materials) and/or non-photosensitive source of reducible silver ions. It can also mean a layer of the material that contains, in addition to the photosensitive silver halide and/or non-photosensitive source of reducible ions, additional essential components and/or desirable additives such as the reducing agent(s). These layers are usually on what is known as the "frontside" of the support but they can be on both sides of the support.

In addition, "frontside" also generally means the side of a thermally developable material that is first exposed to imaging radiation, and "backside" generally refers to the opposite side of the thermally developable material.

"Photocatalyst" means a photosensitive compound such as silver halide that, upon exposure to radiation, provides a compound that is capable of acting as a catalyst for the subsequent development of the thermally developable material.

Many of the materials used herein are provided as a solution. The term "active ingredient" means the amount or the percentage of the desired material contained in a sample. All amounts listed herein are the amount of active ingredient added.

"Ultraviolet region of the spectrum" refers to that region of the spectrum less than or equal to 410 nm, and preferably from about 100 nm to about 410 nm, although parts of these ranges may be visible to the naked human eye. More preferably, the ultraviolet region of the spectrum is the region of from about 190 nm to about 405 nm.

"Visible region of the spectrum" refers to that region of the spectrum of from about 400 nm to about 700 nm.

"Short wavelength visible region of the spectrum" refers to that region of the spectrum of from about 400 nm to about 450 nm.

"Red region of the spectrum" refers to that region of the spectrum of from about 600 nm to about 700 nm.

“Infrared region of the spectrum” refers to that region of the spectrum of from about 700 nm to about 1400 nm.

“Non-photosensitive” means not intentionally light sensitive.

“Transparent” means capable of transmitting visible light or
5 imaging radiation without appreciable scattering or absorption.

The sensitometric term “absorbance” is another term for optical density (OD).

The sensitometric terms “photospeed,” “speed,” or “photographic speed” (also known as sensitivity), absorbance, contrast, D_{min} , and D_{max} have
10 conventional definitions known in the imaging arts. In photothermographic materials, D_{min} is considered herein as image density achieved when the photothermographic material is thermally developed without prior exposure to radiation. It is the average of eight lowest density values on the exposed side of the fiducial mark. D_{max} is the maximum density of film in the imaged area.

15 “Speed-2” is $\text{Log}1/E + 4$ corresponding to the density value of 1.0 above D_{min} where E is the exposure in ergs/cm^2 .

As used herein, the phrase “organic silver coordinating ligand” refers to an organic molecule capable of forming a bond with a silver atom. Although the compounds so formed are technically silver coordination
20 compounds they are also often referred to as silver salts.

In the compounds described herein, no particular double bond geometry (for example, *cis* or *trans*) is intended by the structures drawn unless otherwise specified. Similarly, in compounds having alternating single and double bonds and localized charges their structures are drawn as a formalism. In reality,
25 both electron and charge delocalization exists throughout the conjugated chain.

As is well understood in this art, for the chemical compounds herein described, substitution is not only tolerated, but is often advisable and various substituents are anticipated on the compounds used in the present invention unless otherwise stated. Thus, when a compound is referred to as
30 “having the structure” of, or as “a derivative” of, a given formula, any substitution that does not alter the bond structure of the formula or the shown atoms within

that structure is included within the formula, unless such substitution is specifically excluded by language.

As a means of simplifying the discussion and recitation of certain substituent groups, the term "group" refers to chemical species that may be substituted as well as those that are not so substituted. Thus, the term "alkyl group" is intended to include not only pure hydrocarbon alkyl chains, such as methyl, ethyl, *n*-propyl, *t*-butyl, cyclohexyl, *iso*-octyl, and octadecyl, but also alkyl chains bearing substituents known in the art, such as hydroxyl, alkoxy, phenyl, halogen atoms (F, Cl, Br, and I), cyano, nitro, amino, and carboxy. For example, alkyl group includes ether and thioether groups (for example $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-}$ and $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-S-CH}_2\text{-}$), hydroxyalkyl (such as 1,2-dihydroxyethyl), haloalkyl, nitroalkyl, alkylcarboxy, carboxyalkyl, carboxamido, sulfoalkyl, and other groups readily apparent to one skilled in the art. Substituents that adversely react with other active ingredients, such as very strongly electrophilic or oxidizing substituents, would, of course, be excluded by the ordinarily skilled artisan as not being inert or harmless.

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Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, examples, and claims provided in this application.

25 The Photocatalyst

The photothermographic materials of the present invention include one or more photocatalysts in the photothermographic emulsion layer(s). Useful photocatalysts are typically photosensitive silver halides such as silver bromide, silver iodide, silver chloride, silver bromiodide, silver chlorobromiodide, silver chlorobromide, and others readily apparent to one skilled in the art. Mixtures of silver halides can also be used in any suitable proportion. Silver bromide and

silver bromoiodide are more preferred silver halides, with the latter silver halide having up to 10 mol% silver iodide based on total silver halide.

In some embodiments, higher amounts of iodide may be present in the photosensitive silver halide grains up to the saturation limit of iodide as
5 described in copending and commonly assigned U.S. Serial No. 10/246,265 (filed September 18, 2002 by Maskasky and Scaccia).

The silver halide grains may have any crystalline habit or morphology including, but not limited to, cubic, octahedral, tetrahedral, orthorhombic, rhombic, dodecahedral, other polyhedral, tabular, laminar, twinned,
10 or platelet morphologies and may have epitaxial growth of crystals thereon. If desired, a mixture of grains with different morphologies can be employed. Silver halide grains having cubic and tabular morphology (or both) are preferred. More preferably, the silver halide grains are predominantly (at least 50% based on total silver halide) present as tabular grains.

15 The silver halide grains may have a uniform ratio of halide throughout. They may have a graded halide content, with a continuously varying ratio of, for example, silver bromide and silver iodide, or they may be of the core-shell type, having a discrete core of one or more silver halides, and a discrete shell of one of more different silver halides. Core-shell silver halide grains useful
20 in photothermographic materials and methods of preparing these materials are described for example in U.S. Patent 5,382,504 (Shor et al.), incorporated herein by reference. Iridium and/or copper doped core-shell and non-core-shell grains are described in U.S. Patent 5,434,043 (Zou et al.) and U.S. Patent 5,939,249 (Zou), both incorporated herein by reference.

25 In some instances, it may be helpful to prepare the photosensitive silver halide grains in the presence of a hydroxytetraazaindene or an N-heterocyclic compound comprising at least one mercapto group as described in U.S. Patent 6,413,710 (Shor et al.), that is incorporated herein by reference.

The photosensitive silver halide can be added to (or formed within)
30 the emulsion layer(s) in any fashion as long as it is placed in catalytic proximity to the non-photosensitive source of reducible silver ions.

It is preferred that the silver halide grains be preformed and prepared by an *ex-situ* process, and then be added to and physically mixed with the non-photosensitive source of reducible silver ions.

It is also possible to form the source of reducible silver ions in the presence of *ex-situ*-prepared silver halide. In this process, the source of reducible silver ions, such as a silver salt of an imino compound, is formed in the presence of the preformed silver halide grains. Co-precipitation of the reducible source of silver ions in the presence of silver halide provides a more intimate mixture of the two materials [see, for example U.S. Patent 3,839,049 (Simons)] to provide a “preformed emulsion.”

It is also effective to use an *in-situ* process in which a halide- or halogen-containing compound is added to an organic silver salt to partially convert the silver of the organic silver salt to silver halide. Inorganic halides (such as zinc bromide, calcium bromide, lithium bromide, or zinc iodide) or an organic halogen-containing compound (such as N-bromosuccinimide or pyridinium hydrobromide perbromide) can be used. The details of such *in-situ* generation of silver halide are well known and described for example in U.S. Patent 3,457,075 (Morgan et al.).

Additional methods of preparing these silver halide and organic silver salts and manners of blending them are described in *Research Disclosure*, June 1978, item 17029, U.S. Patent 3,700,458 (Lindholm) and U.S. Patent 4,076,539 (Ikenoue et al.), JP Kokai 49-013224, (Fuji), JP Kokai 50-017216 (Fuji), and JP Kokai 51-042529 (Fuji).

In general, the non-tabular silver halide grains used in this invention can vary in average diameter of up to several micrometers (μm) and they usually have an average particle size of from about 0.01 to about 1.5 μm (preferably from about 0.03 to about 1.0 μm , and more preferably from about 0.05 to about 0.8 μm).

The average size of the photosensitive silver halide grains is expressed by the average diameter if the grains are spherical, and by the average of the diameters of equivalent circles for the projected images if the grains are

cubic, tabular, or other non-spherical shapes. Representative grain sizing methods are described by in "Particle Size Analysis," ASTM Symposium on Light Microscopy, R. P. Loveland, 1955, pp. 94-122, and in C. E. K. Mees and T. H. James, *The Theory of the Photographic Process*, Third Edition, Macmillan, New York, 1966, Chapter 2. Particle size measurements may be expressed in terms of the projected areas of grains or approximations of their diameters. These will provide reasonably accurate results if the grains of interest are substantially uniform in shape.

In most preferred embodiments of this invention, the silver halide grains are provided predominantly (based on at least 50 mol % silver) as tabular silver halide grains that are considered "ultrathin" and have an average thickness of at least 0.02 μm and up to and including 0.10 μm (preferably, an average thickness of at least 0.03 μm and more preferably of at least 0.04 μm , and up to and including 0.08 μm and more preferably up to and including 0.07 μm).

In addition, these ultrathin tabular grains have an equivalent circular diameter (ECD) of at least 0.5 μm (preferably at least 0.75 μm , and more preferably at least 1 μm). The ECD can be up to and including 8 μm (preferably up to and including 6 μm , and more preferably up to and including 4 μm).

The aspect ratio of the useful tabular grains is at least 5:1 (preferably at least 10:1, and more preferably at least 15:1) and generally up to 50:1.

The grain size of ultrathin tabular grains may be determined by any of the methods commonly employed in the art for particle size measurement, such as those described above.

The ultrathin tabular silver halide grains can also be doped using one or more of the conventional metal dopants known for this purpose including those described in *Research Disclosure* item 38957, September, 1996 and U.S. Patent 5,503,970 (Olm et al.), incorporated herein by reference. Preferred dopants include iridium (III or IV) and ruthenium (II or III) salts.

Mixtures of both *in-situ* and *ex-situ* silver halide grains may be used.

The one or more light-sensitive silver halides used in the photo-thermographic materials of the present invention are preferably present in an amount of from about 0.005 to about 0.5 mole (more preferably from about 0.01 to about 0.25 mole, and most preferably from about 0.03 to about 0.15 mole) per mole of non-photosensitive source of reducible silver ions.

Chemical Sensitizers

The photosensitive silver halides used in photothermographic materials of this invention can be chemically sensitized using any useful compound that contains sulfur, tellurium, or selenium, or may comprise a compound containing gold, platinum, palladium, ruthenium, rhodium, iridium, or combinations thereof, a reducing agent such as a tin halide or a combination of any of these. The details of these materials are provided for example, in T. H. James, *The Theory of the Photographic Process*, Fourth Edition, Eastman Kodak Company, Rochester, NY, 1977, Chapter 5, pp. 149-169. Suitable conventional chemical sensitization procedures and compounds are also described in U.S. Patent 1,623,499 (Sheppard et al.), U.S. Patent 2,399,083 (Waller et al.), U.S. Patent 3,297,447 (McVeigh), U.S. Patent 3,297,446 (Dunn), U.S. Patent 5,049,485 (Deaton), U.S. Patent 5,252,455 (Deaton), U.S. Patent 5,391,727 (Deaton), U.S. Patent 5,912,111 (Lok et al.), U.S. Patent 5,759,761 (Lushington et al.), U.S. Patent 6,296,998 (Eikenberry et al.), EP 0 915 371 A1 (Lok et al.), and U.S. Patent 5,691,127 (Daubendiek et al.), all incorporated herein by reference.

Certain substituted or and unsubstituted thioureas can be used as chemical sensitizers including those described in U.S. Patent 6,296,998 (Eikenberry et al.) and U.S. Patent 6,322,961 (Lam et al.), U.S. Patent 4,810,626 (Burgmaier et al.), and U.S. Patent 6,368,779 (Lynch et al.), all of the which are incorporated herein by reference.

Still other useful chemical sensitizers include tellurium- and selenium-containing compounds that are described in U.S. Published Application 2002-0164549 (Lynch et al.), U.S. Patents 5,158,892 (Sasaki et al.), 5,238,807

(Sasaki et al.), 5,942,384 (Arai et al.) and 6,620,577 (Lynch et al.), all of which are incorporated herein by reference.

Noble metal sensitizers for use in the present invention include gold, platinum, palladium and iridium. Gold (+1 or +3) sensitization is particularly preferred, and described in U.S. Patents 5,858,637 (Eshelman et al.) and 5,759,761 (Lushington et al.). Combinations of gold(III) compounds and either sulfur- or tellurium-containing compounds are useful as chemical sensitizers and are described in U.S. Patent 6,423,481 (Simpson et al.). All of the above references are incorporated herein by reference.

In addition, sulfur-containing compounds can be decomposed on silver halide grains in an oxidizing environment. Examples of such sulfur-containing compounds include sulfur-containing spectral sensitizing dyes described in U.S. Patent 5,891,615 (Winslow et al.) and diphenylphosphine sulfide compounds represented by the Structure (PS) described in copending and commonly assigned U.S.S.N. 10/731,251 (filed December 9, 2003 by Simpson, Burleva, and Sakizadeh), both of which are incorporated herein by reference.

The chemical sensitizers can be used in making the silver halide emulsions in conventional amounts that generally depend upon the average size of the silver halide grains. Generally, the total amount is at least 10^{-10} mole per mole of total silver, and preferably from about 10^{-8} to about 10^{-2} mole per mole of total silver. The upper limit can vary depending upon the compound(s) used, the level of silver halide, and the average grain size and grain morphology.

Spectral Sensitizers

The photosensitive silver halides used in the photothermographic features of the invention may be spectrally sensitized with one or more spectral sensitizing dyes that are known to enhance silver halide sensitivity to ultraviolet, visible, and/or infrared radiation. Non-limiting examples of sensitizing dyes that can be employed include cyanine dyes, merocyanine dyes, complex cyanine dyes, complex merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes, and hemioxanol dyes. They may be added at any stage in chemical finishing

of the photothermographic emulsion, but are generally added after chemical sensitization is achieved.

Suitable sensitizing dyes such as those described in U.S. Patent 3,719,495 (Lea), U.S. Patent 4,396,712 (Kinoshita et al.), U.S. Patent 4,439,520 (Kofron et al.), U.S. Patent 4,690,883 (Kubodera et al.), U.S. Patent 4,840,882 (Iwagaki et al.), U.S. Patent 5,064,753 (Kohno et al.), U.S. Patent 5,281,515 (Delprato et al.), U.S. Patent 5,393,654 (Burrows et al.), U.S. Patent 5,441,866 (Miller et al.), U.S. Patent 5,508,162 (Dankosh), U.S. Patent 5,510,236 (Dankosh), U.S. Patent 5,541,054 (Miller et al.), JP Kokai 2000-063690 (Tanaka et al.), JP Kokai 2000-112054 (Fukusaka et al.), JP Kokai 2000-273329 (Tanaka et al.), JP Kokai 2001-005145 (Arai), JP Kokai 2001-064527 (Oshiyama et al.), and JP Kokai 2001-154305 (Kita et al.), can be used in the practice of the invention. All of the publications noted above are incorporated herein by reference. Useful spectral sensitizing dyes are also described in *Research Disclosure*, item 308119, Section IV, December, 1989.

Teachings relating to specific combinations of spectral sensitizing dyes also provided in U.S. Patent 4,581,329 (Sugimoto et al.), U.S. Patent 4,582,786 (Ikeda et al.), U.S. Patent, U.S. Patent 4,609,621 (Sugimoto et al.), U.S. Patent 4,675,279 (Shuto et al.), U.S. Patent 4,678,741 (Yamada et al.), U.S. Patent 4,720,451 (Shuto et al.), U.S. Patent 4,818,675 (Miyasaka et al.), U.S. Patent 4,945,036 (Arai et al.), and U.S. Patent 4,952,491 (Nishikawa et al.). All of the above publications and patents are incorporated herein by reference.

Also useful are spectral sensitizing dyes that decolorize by the action of light or heat as described in U.S. Patent 4,524,128 (Edwards et al.), JP Kokai 2001-109101 (Adachi), JP Kokai 2001-154305 (Kita et al.), and JP 2001-183770 (Hanyu et al.).

Dyes may also be selected for the purpose of supersensitization to attain much higher sensitivity than the sum of sensitivities that can be achieved by using each dye alone.

An appropriate amount of spectral sensitizing dye added is generally about 10^{-10} to 10^{-1} mole, and preferably, about 10^{-7} to 10^{-2} mole per mole of silver halide.

5 **Non-Photosensitive Source of Reducible Silver Ions**

The non-photosensitive source of reducible silver ions used in the thermally developable materials of this invention can be any metal-organic compound that contains reducible silver(I) ions. Such compounds are generally organic silver salts of coordination ligands that are comparatively stable to light
10 and form a silver image when heated to 50°C or higher in the presence of an exposed silver halide (for photothermographic materials) and a reducing agent.

Silver salts of nitrogen-containing heterocyclic compounds are preferred, and one or more silver salts of compounds containing an imino group are particularly preferred, especially in the aqueous-based materials that are
15 preferred in this invention. Representative compounds of this type include, but are not limited to, silver salts of benzotriazole and substituted derivatives thereof (for example, silver methylbenzotriazole and silver 5-chlorobenzotriazole), silver salts of 1,2,4-triazoles or 1-*H*-tetrazoles such as phenylmercaptotetrazole as described in U.S. Patent 4,220,709 (deMauriac), and silver salts of imidazole and
20 imidazole derivatives as described in U.S. Patent 4,260,677 (Winslow et al.). Particularly useful silver salts of this type are the silver salts of benzotriazole, substituted derivatives thereof, or mixtures of two or more of these salts. A silver salt of benzotriazole is most preferred in the photothermographic emulsions and materials of this invention.

25 Other silver salts can be used if present in "minor" amounts (less than 50 mol %) based on the total moles of organic silver salts.

Silver salts of heterocyclic compounds containing mercapto or thione groups and derivatives thereof can also be used. Such heterocyclic nuclei include, but are not limited to, triazoles, oxazoles, thiazoles, thiazolines,
30 imidazoles, diazoles, pyridines, and triazines as described in U.S. Patent 4,123,274 (Knight et al.) and U.S. Patent 3,785,830 (Sullivan et al.). Examples of

other useful silver salts of mercapto or thione substituted compounds that do not contain a heterocyclic nucleus include silver salts of thioglycolic acids, silver salts of dithiocarboxylic acids, and silver salts of thioamides.

Silver salts of organic acids including silver salts of long-chain
5 aliphatic or aromatic carboxylic acids may also be included in minor amounts. The chains typically contain 10 to 30, and preferably 15 to 28, carbon atoms. Silver behenate is a preferred silver carboxylate, alone or mixed with other silver carboxylates.

Sources of reducible silver ions can also be core-shell silver salts as
10 described in U.S. Patent 6,355,408 (Whitcomb et al.), that is incorporated herein by reference wherein a core has one or more silver salts and a shell has one or more different silver salts.

Other useful sources of non-photosensitive reducible silver ions are the silver dimer compounds that comprise two different silver salts as described in
15 U.S. Patent 6,566,045 (Whitcomb), that is incorporated herein by reference.

Still other useful sources of non-photosensitive reducible silver ions in the practice of this invention are the silver core-shell compounds comprising a primary core comprising one or more photosensitive silver halides, or one or more non-photosensitive inorganic metal salts or non-silver containing
20 organic salts, and a shell at least partially covering the primary core, wherein the shell comprises one or more non-photosensitive silver salts, each of which silver salts comprises a organic silver coordinating ligand. Such compounds are described in copending and commonly assigned U.S. Serial No. 10/208,603 (filed July 30, 2002 by Bokhonov, Burleva, Whitcomb, Howlader, and Leichter) that is
25 incorporated herein by reference.

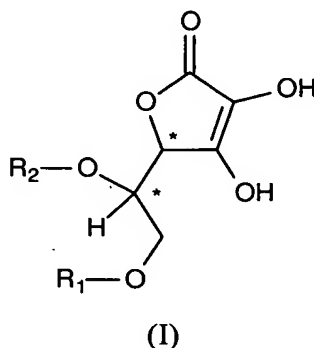
The one or more non-photosensitive sources of reducible silver ions are preferably present in an amount of about 5% by weight to about 70% by weight, and more preferably, about 10% to about 50% by weight, based on the total dry weight of the emulsion layers. Alternatively, the amount of the sources
30 of reducible silver ions is generally present in an amount of from about 0.001 to

about 0.2 mol/m² of the dry photothermographic material (preferably from about 0.01 to about 0.05 mol/m²).

The total amount of silver (from all silver sources) in the photothermographic materials of this invention is generally at least 0.002 mol/m² and preferably from about 0.01 to about 0.05 mol/m². The amount of silver in the thermographic materials of this invention is generally 0.02 mol/m².

Reducing Agents

The reducing agents (or "developers") useful in this invention are ascorbic acid compounds (or derivatives) that are represented by the following Structure (I):



wherein R₁ and R₂ are independently hydrogen and/or the same or different acyl groups [R₃-(C=O)- or R₃-L-(C=O)-], provided that R₁ and R₂ are not both hydrogen. The acyl groups each have 11 or fewer carbon atoms, and preferably each acyl group is branched and/or contains at least one ring. The acyl groups may be substituted with functional groups such as ethers, halogens, esters and amides.

R₃ of the acyl group may be hydrogen, or a substituted or unsubstituted alkyl group having 10 or fewer carbon atoms (such as methyl, ethyl, *iso*-propyl, *t*-butyl, and benzyl), substituted or unsubstituted aryl having 6 to 10 carbon atoms in the carbocyclic ring (such as phenyl, 4-methylphenyl, 4-methoxyphenyl, and naphthyl), substituted or unsubstituted alkenyl having 10 or fewer

carbon atoms in the chain (such as ethenyl, hexenyl, and 1-methylpropenyl), or a substituted or unsubstituted heterocyclic group having 5 to 7 nitrogen, oxygen, sulfur, and carbon atoms in the heterocyclic ring (such as tetrahydrofuryl and benzthiazoyl). L may be oxy, thio, or -NR₄-, wherein R₄ is defined in the same way as R₃.

At least one of R₁ and R₂ is an acyl group and the other of R₁ and R₂ is preferably hydrogen. Preferably, R₃ is *tert*-butyl, R₄ is hydrogen, and L is nitrogen.

Mixtures of these compounds can be used if desired in any specific proportion.

Compounds of Structure I have two chiral centers (indicated by *). Therefore four isomers are possible and compounds of Structure I may be derived from D- or L-ascorbic acid or from D- or L-isoascorbic acid.

Representative examples of compounds having Structure I are shown below in TABLE I.

TABLE I

Compound	Derived From	R ₁	R ₂
I-1	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-2	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	H
I-3	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-4	D-isoascorbic acid	<i>t</i> -Butyl-(C=O)-	<i>t</i> -Butyl-(C=O)-
I-5	D-isoascorbic acid	H	<i>t</i> -Butyl-(C=O)-
I-6	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	H
I-7	L-ascorbic acid	Ph-(C=O)-	H
I-8	L-ascorbic acid	1-Adamantyl-(C=O)-	H
I-9	L-ascorbic acid	1-Adamantylmethyl-(C=O)-	H
I-10	L-ascorbic acid	1-Methylcyclohexyl-(C=O)-	H
I-11	L-ascorbic acid	2-Adamantylmethyl-(C=O)	H

I-12	L-ascorbic acid	2,2-Dimethylpropyl-(C=O)-	H
I-13	L-ascorbic acid	Cyclohexyl-(C=O)-	H
I-14	L-ascorbic acid	1,1-Dimethylpropyl-(C=O)-	H
I-15	L-ascorbic acid	1-Ethylpropyl-(C=O)-	H
I-16	L-ascorbic acid	2,4,4-Trimethylpentyl-(C=O)-	H
I-17	L-ascorbic acid	2-Methylpropyl-(C=O)-	H
I-18	L-ascorbic acid	Cyclopentyl-(C=O)-	H
I-19	L-ascorbic acid	Diethylamino-(C=O)	H
I-20	L-ascorbic acid	Diethylamino-(C=O)-	Diethylamino-(C=O)-
I-21	L-ascorbic acid	Phenyl-NH-(C=O)-	H
I-22	L-ascorbic acid	Hexyl-NH-(C=O)-	Hexyl-NH-(C=O)-
I-23	L-ascorbic acid	<i>t</i> -Butyl-(C=O)-	Ethyl-(C=O)-
I-24	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-
I-25	L-ascorbic acid	Ethyl-O-(C=O)-	H
I-26	L-ascorbic acid	Phenyl-O-(C=O)-	H
I-27	L-ascorbic acid	4-HO-Phenyl-(C=O)-	H
I-28	L-ascorbic acid	2-norbornylmethyl-(C=O)-	H
I-29	L-ascorbic acid	3,4-(HO) ₂ -Phenyl-(C=O)-	H
I-30	L-ascorbic acid	<i>i</i> -Propyl-(C=O)-	<i>i</i> -Propyl-(C=O)-
I-31	L-ascorbic acid	Ethyl-(C=O)-	Ethyl-(C=O)-

Compounds I-1, I-2, I-7, and I-9 are preferred.

Compounds of Structure I may be prepared by known methods.

For example, 5- and/or 6-substituted esters of ascorbic acid may be prepared by
5 the reaction of ascorbic acid and a carboxylic acid in sulfuric acid as described by
H. Tanaka and R. Yamamoto, *Yakugaku Zasshi*, **1966**, 86(5), 376-83. In particular,
compound I-1 has been prepared using this method by K.R. Bharucha et al.
J. Agric. Food Chem., **1980**, 28(6), 1274-181. The preparation of 5- or 6-acyl

ascorbic acid derivatives has also been accomplished through the use of enzymes as described, for example, in T. Maugard et al., *Biotechnology Progress*, **2000**, *16*(3), 358-362, Y. Watanabe et al., *Food Sci. Technol. Res.*, **1999**, *5*(2), 188-192, U.S. Patent 5,079,153 (Enomoto et al.), and WO 03/018,003 (Rath et al.).

5 Alternatively, 2-O,3-O-dibenzyl-ascorbic acid can be prepared as described by R. Dallacker and F. Sanders, *Chemiker-Zeitung*, **1985**, *109*(6), 197-202. Acylation of this material and removal of the benzyl groups by hydrogenation affords 5-acyl, 6-acyl, or 5,6-diacyl ascorbic acid derivatives. Mixed acyl derivatives can be prepared in this manner. 5,6-Diacyl ascorbic acid derivatives have also been
10 prepared using methods described in JP 49-87655 (Shionogi & Co. Ltd.), and U.S. Patent 4,822,898 (Kamaya et al.).

Minor (less than 20 mol % of total moles of reducing agents) of conventional reducing agents [such as ascorbic acid or ascorbic acid derivatives not represented by Structure (I) or hindered phenols] can be used in combination
15 with the reducing agents of Structure (I) if desired, but it is preferred that the materials of this invention contain the compounds of Structure (I) as the exclusive reducing agents.

If desired, co-developers and contrast enhancing agents may be used in combination with the ascorbic acid and reductone reducing agents
20 described herein. Useful co-developer reducing agents include for example, those described in U.S. Patent 6,387,605 (Lynch et al.) that is incorporated herein by reference.

Additional classes of reducing agents that may be used as co-developers are trityl hydrazides and formyl phenyl hydrazides as described in
25 U.S. Patent 5,496,695 (Simpson et al.), 2-substituted malondialdehyde compounds as described in U.S. Patent 5,654,130 (Murray), and 4-substituted isoxazole compounds as described in U.S. Patent 5,705,324 (Murray). Additional developers are described in U.S. Patent 6,100,022 (Inoue et al.). All of the patents above are incorporated herein by reference.

30 Yet another class of co-developers includes substituted acrylonitrile compounds that are identified as HET-01 and HET-02 in U.S. Patent 5,635,339

(Murray) and CN-01 through CN-13 in U.S. Patent 5,545,515 (Murray et al.), both incorporated herein by reference.

Various contrast enhancing agents may be used in some photo-thermographic materials with specific co-developers. Examples of useful contrast enhancing agents include, but are not limited to, hydroxylamines (including hydroxylamine and alkyl- and aryl-substituted derivatives thereof), alkanolamines and ammonium phthalamate compounds as described in U.S. Patent 5,545,505 (Simpson), hydroxamic acid compounds as described in U.S. Patent 5,545,507 (Simpson et al.), N-acylhydrazine compounds as described in U.S. Patent 5,558,983 (Simpson et al.), and hydrogen atom donor compounds as described in U.S. Patent 5,637,449 (Harring et al.). All of the patents above are incorporated herein by reference.

The reducing agent (or mixture thereof) of Structure (I) is generally present in the thermally developable compositions of this invention in an amount of from about 0.3 to about 1.0 mol/mol of total silver. In the thermally developable materials of this invention, these reducing agents are generally present in an amount of from about 0.002 to about 0.05 mol/m² (preferably from about 0.006 to about 0.03 mol/m²).

Other Addenda

The thermally developable materials of this invention can also include one or more compounds that are known in the art as "toners." Toners are compounds that when added to the imaging layer shift the color of the developed silver image from yellowish-orange to brown-black or blue-black, and/or act as development accelerators to speed up thermal development. "Toners" or derivatives thereof that improve the black-and-white image are highly desirable components of the thermally developable materials of this invention.

Thus, compounds that either act as toners or react with a reducing agent to provide toners can be present in an amount of about 0.01% by weight to about 10% (preferably from about 0.1% to about 10% by weight) based on the total dry weight of the layer in which they are included. The amount can also be

defined as being within the range of from about 1×10^{-5} to about 1.0 mol per mole of non-photosensitive source of reducible silver in the photothermographic material. The toner compounds may be incorporated in one or more of the thermally developable layers as well as in adjacent layers such as a protective overcoat layer or underlying "carrier" layer. Toners can be located on both sides of the support if thermally developable layers are present on both sides of the support.

Compounds useful as toners are described, for example, in U.S. Patent 3,074,809 (Owen), U.S. Patent 3,080,254 (Grant, Jr.), U.S. Patent 3,446,648 (Workman), U.S. Patent 3,844,797 (Willems et al.), U.S. Patent 3,847,612 (Winslow), U.S. Patent 3,951,660 (Hagemann et al.), U.S. Patent 4,082,901 (Laridon et al.), U.S. Patent 4,123,282 (Winslow), U.S. Patent 5,599,647 (Defieuw et al.), U.S. Patent 3,832,186 (Masuda et al.), and GB 1,439,478 (AGFA).

Particularly useful toners are mercaptotriazoles as described in copending and commonly assigned U.S. Serial No. 10/193,443 (filed July 11, 2002 by Lynch, Zou, and Ulrich), the heterocyclic disulfide compounds described in copending and commonly assigned U.S. Serial No. 10/384,244 (filed March 7, 2003 by Lynch and Ulrich), the triazine-thione compounds described in copending and commonly assigned U.S. Serial No. 10/341,754 (filed January 14, 2003 by Lynch, Ulrich, and Skoug). All of the above are incorporated herein by reference.

Also useful as toners are phthalazine and phthalazine derivatives [such as those described in U.S. Patent 6,146,822 (Asanuma et al.) incorporated herein by reference], phthalazinone, and phthalazinone derivatives as well as phthalazinium compounds [such as those described in U.S. Patent 6,605,418 (Ramsden et al.), incorporated herein by reference].

The photothermographic materials of this invention can also contain other additives such as shelf-life stabilizers, antifoggants, contrast enhancing agents, development accelerators, acutance dyes, post-processing stabilizers or stabilizer precursors, thermal solvents (also known as melt formers),

humectants, and other image-modifying agents as would be readily apparent to one skilled in the art.

To further control the properties of photothermographic materials (for example, contrast, D_{\min} , speed, or fog) in infrared sensitive materials, it may
5 be preferable to add one or more heteroaromatic mercapto compounds or heteroaromatic disulfide compounds of the formulae Ar-S-M^1 and Ar-S-S-Ar , wherein M^1 represents a hydrogen atom or an alkali metal atom and Ar represents a heteroaromatic ring or fused heteroaromatic ring containing one or more of nitrogen, sulfur, oxygen, selenium, or tellurium atoms. Useful heteroaromatic
10 mercapto compounds are described as supersensitizers in EP 0 559 228 B1 (Philip et al.).

The photothermographic materials of the present invention can be further protected against the production of fog and can be stabilized against loss of sensitivity during storage. Suitable antifoggants and stabilizers that can be used
15 alone or in combination include thiazolium salts as described in U.S. Patent 2,131,038 (Brooker et al.) and U.S. Patent 2,694,716 (Allen), azaindenes as described in U.S. Patent 2,886,437 (Piper), triazaindolizines as described in U.S. Patent 2,444,605 (Heimbach), urazoles as described in U.S. Patent 3,287,135 (Anderson), sulfocatechols as described in U.S. Patent 3,235,652 (Kennard),
20 oximes as described in GB 623,448 (Carrol et al.), polyvalent metal salts as described in U.S. Patent 2,839,405 (Jones), thiuronium salts as described in U.S. Patent 3,220,839 (Herz), palladium, platinum, and gold salts as described in U.S. Patent 2,566,263 (Tirelli) and U.S. Patent 2,597,915 (Damshroder), compounds having $-\text{SO}_2\text{CBr}_3$ groups as described for example in U.S. Patent 5,594,143 (Kirk et al.) and U.S. Patent 5,374,514 (Kirk et al.), and 2-(tribromomethylsulfonyl)-
25 quinoline compounds as described in U.S. Patent 5,460,938 (Kirk et al.).

Stabilizer precursor compounds capable of releasing stabilizers upon application of heat during development can also be used as described in U.S. Patent 5,158,866 (Simpson et al.), U.S. Patent 5,175,081 (Krepski et al.), U.S.
30 Patent 5,298,390 (Sakizadeh et al.), and U.S. Patent 5,300,420 (Kenney et al.).

In addition, certain substituted-sulfonyl derivatives of benzo-triazoles (for example alkylsulfonylbenzotriazoles and arylsulfonylbenzotriazoles) have been found to be useful for post-processing print stabilizing as described in U.S. Patent 6,171,767 (Kong et al.).

5 Other useful antifoggants/stabilizers are described in U.S. Patent 6,083,681 (Lynch et al.). Still other antifoggants are hydrobromic acid salts of heterocyclic compounds (such as pyridinium hydrobromide perbromide) as described in U.S. Patent 5,028,523 (Skoug), benzoyl acid compounds as described in U.S. Patent 4,784,939 (Pham), substituted propenenitrile compounds as
10 described in U.S. Patent 5,686,228 (Murray et al.), silyl blocked compounds as described in U.S. Patent 5,358,843 (Sakizadeh et al.), vinyl sulfones as described in U.S. Patent 6,143,487 (Philip, et al.), diisocyanate compounds as described in EP 0 600 586A1 (Philip et al.), and tribromomethylketones as described in EP 0 600 587A1 (Oliff et al.).

15 The photothermographic materials may also include one or more polyhalo antifoggants that include one or more polyhalo substituents including but not limited to, dichloro, dibromo, trichloro, and tribromo groups. The antifoggants can be aliphatic, alicyclic or aromatic compounds, including aromatic heterocyclic and carbocyclic compounds. Particularly useful antifoggants of this
20 type are polyhalo antifoggants, such as those having a $-SO_2C(X')_3$ group wherein X' represents the same or different halogen atoms.

 Another class of useful antifoggants includes those compounds described in U.S. Patent 6,514,678 (Burgmaier et al.), incorporated herein by reference.

25 Advantageously, the photothermographic materials of this invention also include one or more thermal solvents (also called "heat solvents," "thermosolvents," "melt formers," "melt modifiers," "eutectic formers," "development modifiers," "waxes," or "plasticizers").

 By the term "thermal solvent" in this invention is meant an organic
30 material which becomes a plasticizer or liquid solvent for at least one of the imaging layers upon heating at a temperature above 60°C. Useful for that purpose

are polyethylene glycols having a mean molecular weight in the range of 1,500 to 20,000 described in U.S. Patent 3,347,675 (Henn et al.), urea, methyl sulfonamide and ethylene carbonate as described in U.S. Patent 3,667,959 (Bojara et al.), and compounds described as thermal solvents in *Research Disclosure*, December 5 1976, item 15027, pp. 26-28. Other representative examples of such compounds include, but are not limited to, niacinamide, hydantoin, 5,5-dimethylhydantoin, salicylanilide, phthalimide, N-hydroxyphthalimide, N-potassium-phthalimide, succinimide, N-hydroxy-1,8-naphthalimide, phthalazine, 1-(2H)-phthalazinone, 2-acetylphthalazinone, benzanilide, 1,3-dimethylurea, 1,3-diethylurea, 10 1,3-diallylurea, *meso*-erythritol, D-sorbitol, tetrahydro-2-pyrimidone, glycouril, 2-imidazolidone, 2-imidazolidone-4-carboxylic acid, and benzenesulfonamide. Combinations of these compounds can also be used including, for example, a combination of succinimide and 1,3-dimethylurea.

It may be advantageous to include a base-release agent or base precursor in the photothermographic materials. Representative base-release 15 agents or base precursors include guanidinium compounds, such as guanidinium trichloroacetate, and other compounds that are known to release a base but do not adversely affect photographic silver halide materials, such as phenylsulfonyl acetates as described in U.S. Patent 4,123,274 (Knight et al.).

20 **Phosphors**

In some embodiments, it is also effective to incorporate X-radiation-sensitive phosphors in the chemically sensitized photothermographic emulsions and materials of this invention as described in U.S. Patents 6,573,033 25 (Simpson et al.) and 6,440,649 (Simpson et al.), both of which are incorporated herein by reference.

Any conventional or useful storage or prompt-emitting phosphor can be used, singly or in mixtures, in the practice of this invention.

The one or more phosphors used in the practice of this invention 30 are present in the photothermographic materials in an amount of at least 0.1 mole per mole, and preferably from about 0.5 to about 20 mole, per mole of total silver

in the photothermographic material. Generally, the amount of total silver is at least 0.002 mol/m².

Because of the size of the phosphors used in the invention, generally the layers in which they are incorporated (usually one or more emulsion
5 layers) have a dry coating weight of at least 5 g/m², and preferably from about 5 g/m², to about 200 g/m². Most preferably, the one or more phosphors and the photosensitive silver halide are incorporated within the same imaging layer that has a dry coating weight within the noted preferred range.

10 **Binders**

The photosensitive silver halide (if present), the non-photosensitive source of reducible silver ions, the reducing agent, antifoggant(s), toner(s), and any other additives used in the present invention are added to and coated in one or more binders using a suitable solvent. Thus, organic solvent-based or
15 aqueous-based formulations are used to prepare the thermographic and photothermographic materials of this invention. Mixtures of different types of hydrophilic and/or hydrophobic binders can also be used. Preferably, hydrophilic binders and water-dispersible polymeric latexes are used to provide aqueous-based materials in this invention.

20 Examples of useful hydrophilic binders include, but are not limited to, proteins and protein derivatives, gelatin and gelatin derivatives (hardened or unhardened), cellulosic materials, acrylamide/methacrylamide polymers, acrylic/methacrylic polymers, polyvinyl pyrrolidones, polyvinyl alcohols, poly(vinyl lactams), polymers of sulfoalkyl acrylate or methacrylates, hydrolyzed
25 polyvinyl acetates, polyamides, polysaccharides, and other naturally occurring or synthetic vehicles commonly known for use in aqueous-based photographic emulsions (see for example *Research Disclosure*, item 38957, noted above).

Particularly useful hydrophilic binders are gelatin, gelatin derivatives, polyvinyl alcohols, and cellulosic materials. Gelatin and its
30 derivatives are most preferred, and comprise at least 75 weight % of total binders when a mixture of binders is used.

Aqueous dispersions of water-dispersible polymeric latexes may also be used, alone or with hydrophilic or hydrophobic binders described herein. Such dispersions are described in, for example, U.S. Patent 4,504,575 (Lee), U.S. Patent 6,083,680 (Ito et al), U.S. Patent 6,100,022 (Inoue et al.), U.S. Patent 6,132,949 (Fujita et al.), U.S. Patent 6,132,950 (Ishigaki et al.), U.S. Patent 6,140,038 (Ishizuka et al.), U.S. Patent 6,150,084 (Ito et al.), U.S. Patent 6,312,885 (Fujita et al.), U.S. Patent 6,423,487 (Naoi), all of which are incorporated herein by reference.

In some embodiments, the components needed for imaging can be added to one or more binders that are predominantly (at least 50% by weight of total binders) hydrophobic in nature. Examples of typical hydrophobic binders include polyvinyl acetals, polyvinyl chloride, polyvinyl acetate, cellulose acetate, cellulose acetate butyrate, polyolefins, polyesters, polystyrenes, polyacrylonitrile, polycarbonates, methacrylate copolymers, maleic anhydride ester copolymers, butadiene-styrene copolymers, and other materials readily apparent to one skilled in the art. Copolymers (including terpolymers) are also included in the definition of polymers. The polyvinyl acetals (such as polyvinyl butyral and polyvinyl formal), cellulose ester polymers, and vinyl copolymers (such as polyvinyl acetate and polyvinyl chloride) are preferred. Particularly suitable binders are polyvinyl butyral resins that are available under the name BUTVAR[®] from Solutia, Inc.(St. Louis, MO) and PIOLOFORM[®] from Wacker Chemical Company (Adrian, MI) and cellulose ester polymers.

Hardeners for various binders may be present if desired. Useful hardeners are well known and include diisocyanate compounds as described for example, in EP 0 600 586B1 (Philip et al.) and vinyl sulfone compounds as described in U.S. Patent 6,143,487 (Philip et al.), and EP 0 640 589A1 (Gathmann et al.), aldehydes and various other hardeners as described in U.S. Patent 6,190,822 (Dickerson et al.).

Where the proportions and activities of the photothermographic materials require a particular developing time and temperature, the binder(s) should be able to withstand those conditions. Generally, it is preferred that the

binder does not decompose or lose its structural integrity at 120°C for 60 seconds. It is more preferred that it does not decompose or lose its structural integrity at 177°C for 60 seconds.

5 The polymer binder(s) is used in an amount sufficient to carry the components dispersed therein. Preferably, a binder is used at a level of about 10% by weight to about 90% by weight, and more preferably at a level of about 20% by weight to about 70% by weight, based on the total dry weight of the layer in which it is included. The amount of binders on opposing sides of the support in double-sided materials may be the same or different.

10

Support Materials

The photothermographic materials of this invention comprise a polymeric support that is preferably a flexible, transparent film that has any desired thickness and is composed of one or more polymeric materials. They are
15 required to exhibit dimensional stability during thermal development and to have suitable adhesive properties with overlying layers. Useful polymeric materials for making such supports include, but are not limited to, polyesters (such as polyethylene terephthalate and polyethylene naphthalate), cellulose acetate and other cellulose esters, polyvinyl acetal, polyolefins, polycarbonates, and
20 polystyrenes. Preferred supports are composed of polymers having good heat stability, such as polyesters and polycarbonates. Support materials may also be treated or annealed to reduce shrinkage and promote dimensional stability.

It is also useful to use supports comprising dichroic mirror layers as described in U.S. Patent 5,795,708 (Boutet), incorporated herein by reference.

25

Also useful are transparent, multilayer, polymeric supports comprising numerous alternating layers of at least two different polymeric materials that preferably reflect at least 50% of actinic radiation in the range of wavelengths to which the photothermographic material is sensitive. Such polymeric supports are described in U.S. Patent 6,630,283 (Simpson et al.) that is
30 incorporated herein by reference.

Support materials can contain various colorants, pigments, antihalation or acutance dyes if desired. For example, blue-tinted supports are particularly useful for providing images useful for medical diagnosis. Support materials may be treated using conventional procedures (such as corona
5 discharge) to improve adhesion of overlying layers, or subbing or other adhesion-promoting layers can be used.

Photothermographic Formulations

An organic solvent-based coating formulation for the emulsion
10 layer(s) can be prepared by mixing the emulsion components with one or more hydrophobic binders in a suitable solvent system that usually includes an organic solvent, such as toluene, 2-butanone (methyl ethyl ketone), acetone, or tetrahydrofuran.

Alternatively and preferably, the emulsion components are
15 prepared in a formulation containing a hydrophilic binder (such as gelatin, a gelatin-derivative, or a cellulosic material) or a water-dispersible polymer in the form of a latex in water or water-organic solvent mixtures to provide aqueous-based coating formulations.

The materials of the invention can contain plasticizers and
20 lubricants such as poly(alcohols) and diols as described in U.S. Patent 2,960,404 (Milton et al.), fatty acids or esters as described in U.S. Patents 2,588,765 (Robijns) and 3,121,060 (Duane), and silicone resins as described in GB 955,061 (DuPont). The materials can also contain inorganic or organic matting agents as described in U.S. Patents 2,992,101 (Jelley et al.) and 2,701,245 (Lynn).
25 Polymeric fluorinated surfactants may also be useful in one or more layers as described in U.S. Patent 5,468,603 (Kub).

U.S. Patent 6,436,616 (Geisler et al.), incorporated herein by reference, describes various means of modifying photothermographic materials to reduce what is known as the "woodgrain" effect, or uneven optical density.

30 The materials of this invention can include one or more antistatic agents in any of the layers on either or both sides of the support. Conductive

components include soluble salts, evaporated metal layers, or ionic polymers as described in U.S. Patent 2,861,056 (Minsk) and U.S. Patent 3,206,312 (Sterman et al.), insoluble inorganic salts as described in U.S. Patent 3,428,451 (Trevoy), electroconductive underlayers as described in U.S. Patent 5,310,640 (Markin et al.), electronically-conductive metal antimonate particles as described in U.S. Patent 5,368,995 (Christian et al.), and electrically-conductive metal-containing particles dispersed in a polymeric binder as described in EP 0 678 776 A1 (Melpolder et al.). Particularly useful conductive particles are the non-acicular metal antimonate particles described in copending and commonly assigned U.S. Serial No. 10/304,224 (filed on November 27, 2002 by LaBelle, Sakizadeh, Ludemann, Bhawe, and Pham). All of the above patents and patent applications are incorporated herein by reference.

Still other conductive compositions include one or more fluorochemicals each of which is a reaction product of $R_f\text{-CH}_2\text{CH}_2\text{-SO}_3\text{H}$ with an amine wherein R_f comprises 4 or more fully fluorinated carbon atoms as described in U.S. Published Application 2003-0198901 (Sakizadeh et al.) that is incorporated herein by reference.

Additional conductive compositions include one or more fluorochemicals described in more detail in copending and commonly assigned U.S. Serial No. 10/265,058 (filed October 4, 2002 by Sakizadeh, LaBelle, and Bhawe) that is incorporated herein by reference.

Layers to promote adhesion of one layer to another are also known, as described in U.S. Patent 5,891,610 (Bauer et al.), U.S. Patent 5,804,365 (Bauer et al.), U.S. Patent 4,741,992 (Przedziecki), and U.S. Patent 5,928,857 (Geisler et al.).

Layers to reduce emissions from the film may also be present, including the polymeric barrier layers described in U.S. Patent 6,352,819 (Kenney et al.), U.S. Patent 6,352,820 (Bauer et al.), U.S. Patent 6,420,102 (Bauer et al.), and U.S. Patent 6,667,148 (Rao et al.), and U.S. Serial No. 10/351,814 (filed January 27, 2003 by Hunt), all incorporated herein by reference.

The formulations described herein (including the thermally developable formulations) can be coated by various coating procedures including wire wound rod coating, dip coating, air knife coating, curtain coating, slide coating, or extrusion coating using hoppers of the type described in U.S. Patent 2,681,294 (Beguín). Layers can be coated one at a time, or two or more layers can be coated simultaneously by the procedures described in U.S. Patent 2,761,791 (Russell), U.S. Patent 4,001,024 (Dittman et al.), U.S. Patent 4,569,863 (Keopke et al.), U.S. Patent 5,340,613 (Hanzalik et al.), U.S. Patent 5,405,740 (LaBelle), U.S. Patent 5,415,993 (Hanzalik et al.), U.S. Patent 5,525,376 (Leonard), U.S. Patent 5,733,608 (Kessel et al.), U.S. Patent 5,849,363 (Yapel et al.), U.S. Patent 5,843,530 (Jerry et al.), U.S. Patent 5,861,195 (Bhave et al.), and GB 837,095 (Ilford) all of which are incorporated herein by reference. A typical coating gap for the emulsion layer can be from about 10 to about 750 μm , and the layer can be dried in forced air at a temperature of from about 20°C to about 100°C. It is preferred that the thickness of the layer be selected to provide maximum image densities greater than about 0.2, and more preferably, from about 0.5 to 5.0 or more, as measured by a MacBeth Color Densitometer Model TD 504.

For example, after or simultaneously with application of the emulsion formulation to the support, a protective overcoat formulation can be applied over the emulsion formulation.

Preferably, two or more layer formulations are applied simultaneously to a film support using slide coating, the first layer being coated on top of the second layer while the second layer is still wet, using the same or different solvents.

In other embodiments, a "carrier" layer formulation comprising a single-phase mixture of the two or more polymers described above may be applied directly onto the support and thereby located underneath the emulsion layer(s) as described in U.S. Patent 6,355,405 (Ludemann et al.), incorporated herein by reference. The carrier layer formulation can be applied simultaneously with application of the emulsion layer formulation.

Mottle and other surface anomalies can be reduced in the materials by incorporation of a fluorinated polymer as described for example in U.S. Patent 5,532,121 (Yonkoski et al.) or by using particular drying techniques as described, for example in U.S. Patent 5,621,983 (Ludemann et al.).

5 While the first and second layers can be coated on one side of the film support, manufacturing methods can also include forming on the opposing or backside of the polymeric support, one or more additional layers, including a conductive layer, antihalation layer, or a layer containing a matting agent (such as silica), or a combination of such layers. Alternatively, one backside layer can
10 perform all of the desired functions.

It is also contemplated that the thermally developable materials of this invention can include emulsion layers on both sides of the support and/or an antihalation underlayer beneath at least one emulsion layer.

To promote image sharpness, photothermographic materials of the
15 present invention can contain one or more layers containing acutance and/or antihalation dyes. These dyes are chosen to have absorption close to the exposure wavelength and are designed to absorb scattered light. One or more antihalation compositions may be incorporated into one or more antihalation backing layers, underlayers, or overcoats. Additionally, one or more acutance dyes may be
20 incorporated into one or more frontside layers.

Dyes useful as antihalation and acutance dyes include squaraine dyes described in U.S. Patent 5,380,635 (Gomez et al.), U.S. Patent 6,063,560 (Suzuki et al.), and EP 1 083 459A1 (Kimura), indolenine dyes described in EP 0 342 810A1 (Leichter), and cyanine dyes described in U.S. Published Application
25 2003-0162134 (Hunt et al.), all incorporated herein by reference.

It may also be useful to employ compositions including acutance or antihalation dyes that will decolorize or bleach with heat during processing, as described in, for example, U.S. Patent 5,135,842 (Kitchin et al.), U.S. Patent 5,266,452 (Kitchin et al.), U.S. Patent 5,314,795 (Helland et al.), U.S. Patent
30 6,306,566, (Sakurada et al.), JP Kokai 2001-142175 (Hanyu et al.), and JP Kokai 2001-183770 (Hanyu et al.). Useful bleaching compositions are described in JP

Kokai 11-302550 (Fujiwara), JP Kokai 2001-109101 (Adachi), JP Kokai 2001-51371 (Yabuki et al.), and JP Kokai 2000-029168 (Noro). All of the noted publications are incorporated herein by reference.

Other useful heat-bleachable backside antihalation compositions can include a radiation absorbing compound such as an oxonol dye and various other compounds used in combination with a hexaarylbiimidazole (also known as a "HABI"), or mixtures thereof. HABI compounds are described in U.S. Patent 4,196,002 (Levinson et al.), U.S. Patent 5,652,091 (Perry et al.), and U.S. Patent 5,672,562 (Perry et al.), all incorporated herein by reference. Examples of such heat-bleachable compositions are described for example in U.S. Patent 6,455,210 (Irving et al.), U.S. Patent 6,514,677 (Ramsden et al.), and U.S. Patent 6,558,880 (Goswami et al.), all incorporated herein by reference.

Under practical conditions of use, these compositions are heated to provide bleaching at a temperature of at least 90°C for at least 0.5 seconds (preferably, at a temperature of from about 100°C to about 200°C for from about 5 to about 20 seconds).

In some embodiments, the thermally developable materials of this invention include a surface protective layer over one or more imaging layers on one or both sides of the support. In other embodiments, the materials include a surface protective layer on the same side of the support as the one or more emulsion layers and a layer on the backside that includes an antihalation and/or conductive antistatic composition. A separate backside surface protective layer can also be included in these embodiments.

Imaging/Development

The photothermographic materials of the present invention can be imaged in any suitable manner consistent with the type of material, using any suitable imaging source (typically some type of radiation or electronic signal). In some embodiments, the materials are sensitive to radiation in the range of from about at least 300 nm to about 1400 nm, and preferably from about 300 nm to about 850 nm because of the use of appropriate spectral sensitizing dyes. In one

preferred embodiment, the materials are sensitive to radiation of from about 350 nm to about 450 nm.

Imaging can be achieved by exposing the photothermographic materials of this invention to a suitable source of radiation to which they are
5 sensitive, including ultraviolet radiation, visible light, near infrared radiation and infrared radiation to provide a latent image. Suitable exposure means are well known and include incandescent or fluorescent lamps, xenon flash lamps, lasers, laser diodes, light emitting diodes, infrared lasers, infrared laser diodes, infrared light-emitting diodes, infrared lamps, or any other ultraviolet, visible, or infrared
10 radiation source readily apparent to one skilled in the art such as described in *Research Disclosure*, item 38957 (noted above).

In some embodiments, the photothermographic materials of the present invention can be imaged using an X-radiation imaging source and one or more prompt-emitting or storage X-ray sensitive phosphor screens adjacent to the
15 photothermographic material. The phosphors emit suitable radiation to expose the photothermographic material.

In other embodiments, the photothermographic materials of the present invention can be imaged directly using an X-radiation imaging source to provide a latent image.

20 In still other embodiments, the photothermographic materials of the present invention can be imaged using an X-radiation imaging source and one or more X-ray sensitive prompt emitting or storage phosphors incorporated within the photothermographic material.

Imaging of the thermographic materials of this invention is carried
25 out using a suitable imaging source of thermal energy such as a thermal print head.

Thermal development conditions will vary, depending on the construction used but will typically involve heating the thermally sensitive material at a suitably elevated temperature, for example, at from about 50°C to
30 about 250°C for a sufficient period of time, generally from about 1 to about 120 seconds. Heating can be accomplished using any suitable heating means. A

preferred heat development procedure for photothermographic materials described herein includes heating at from 130°C to about 170°C for from about 10 to about 25 seconds. A particularly preferred development procedure is heating at about 150°C for 15 to 25 seconds.

5

Use as a Photomask

In some embodiments, the photothermographic and thermographic materials of the present invention are sufficiently transmissive in the range of from about 350 to about 450 nm in non-imaged areas to allow their use in a method where there is a subsequent exposure of an ultraviolet or short wavelength visible radiation sensitive imageable medium. The heat-developed materials absorb ultraviolet or short wavelength visible radiation in the areas where there is a visible image and transmit ultraviolet or short wavelength visible radiation where there is no visible image. The materials may then be used as a mask and positioned between a source of imaging radiation (such as an ultraviolet or short wavelength visible radiation energy source) and an imageable material that is sensitive to such imaging radiation, such as a photopolymer, diazo material, photoresist, or photosensitive printing plate. Exposing the imageable material to the imaging radiation through the visible image in the exposed and heat-developed photothermographic material provides an image in the imageable material. These embodiments of the imaging method of this invention are carried out using Steps A through D noted above in the Summary of the Invention.

25

Imaging Assemblies

In preferred embodiments, the photothermographic materials of this invention are used in association with one or more phosphor intensifying screens and/or metal screens in what is known as "imaging assemblies." Double-sided X-radiation sensitive photothermographic materials are preferably used in combination with two adjacent intensifying screens, one screen in the "front" and one screen in the "back" of the material. The front and back screens can be appropriately chosen depending upon the type of emissions desired, the desired

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photicity, emulsion speeds, and percent crossover. A metal (such as copper or lead) screen can also be included if desired.

There are a wide variety of phosphors known in the art that can be formulated into phosphor intensifying screens as described in hundreds of publications including U.S. Patent 6,573,033 (noted above) and references cited therein.

Imaging assemblies can be prepared by arranging a suitable photo-thermographic material in association with one or more phosphor intensifying screens, and one or more metal screens in a suitable holder (often known as a cassette), and appropriately packaging them for transport and imaging uses.

The following examples are provided to illustrate the practice of the present invention and the invention is not meant to be limited thereby.

Materials and Methods for the Examples:

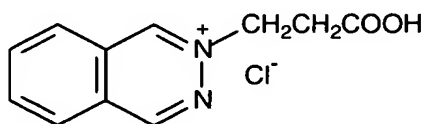
All materials used in the following examples can be prepared using known synthetic procedures or are readily available from standard commercial sources, such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified. All percentages are by weight unless otherwise indicated.

Densitometry measurements were carried out on an X-Rite[®] Model 301 densitometer that is available from X-Rite Inc. (Grandville, MI).

Vinol 523 is partially hydrolyzed (87 to 89%) poly(vinyl alcohol). It was obtained from Air Products and Chemicals, Inc. (Allentown, PA).

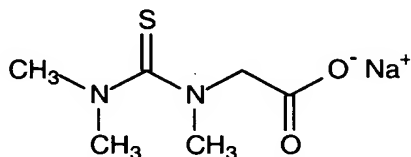
ZONYL[®] FSN is a nonionic fluorosurfactant that is available from E. I. DuPont de Nemours & Co. (Wilmington, DE). It is a fluorinated poly-ethyleneoxide alcohol.

Compound A-1 is described in U.S. Patent 6,605,418 (noted above) and is believed to have the following structure.



(A-1)

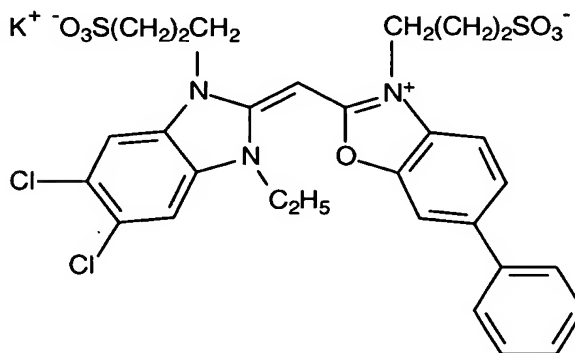
Compound SS-1a is described in U.S. Patent 6,296,998 (Eikenberry et al.) and is believed to have the following structure.



5

(SS-1a)

Blue sensitizing dye SSD-1 is believed to have the following structure.

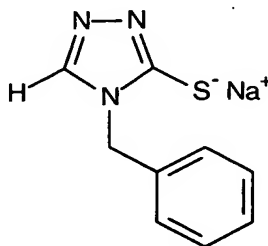


10

(SSD-1)

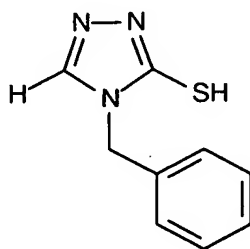
Compound T-1 is the sodium salt of 2,4-dihydro-4-(phenylmethyl)-3H-1,2,4-triazole-3-thione and is believed to have the following structure. It is drawn as the sodium salt of the thiol form but may also exist as the sodium salt of the thione tautomer.

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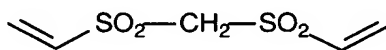
(T-1)

Compound T-2 is 2,4-dihydro-4-(phenylmethyl)-3H-1,2,4-triazole-3-thione. It is believed to have the following structure. It is drawn as the thiol form but may also exist as the thione tautomer.



(T-2)

Bisvinyl sulfonyl methane (VS-1) is 1,1'-(methylenebis(sulfonyl))-bis-ethene and is believed to have the following structure.



(VS-1)

Preparation of Ascorbic Acid Compounds of Structure I

Synthetic Preparation 1: 2-O,3-O-Dibenzyl-L-ascorbic acid,
5-O,6-O-bis(2-methylpropionate) and 2-O,3-O-dibenzyl-L-ascorbic acid,
5-O,6-O-bis(2,2-dimethylpropionate).

To a solution of 10.42 g (29.24 mmol) of 2-O,3-O-dibenzyl-L-ascorbic acid in 60 ml of dry pyridine cooled to 5 °C under nitrogen with magnetic stirring was added 7.79 g (73.10 mmol) of isobutyryl chloride via syringe over 15 min. The mixture was warmed to room temperature, held 18 hr, poured into water, extracted into ethyl acetate, washed 4 times with 1 M hydrochloric acid solution and once with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. HPLC/MS and NMR indicated the desired product. 2-O,3-O-Dibenzyl-L-ascorbic

acid, 5-O,6-O-bis(2,2-dimethylpropionate) was also prepared in an analogous manner substituting 2,2-dimethylpropionyl chloride for isobutyryl chloride.

Synthetic Preparation 2: L-ascorbic acid, 5-O,6-O-bis(2-methylpropionate)
(Compound I-30) and L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate)

5 (Compound I-3).

The product obtained in Synthetic Preparation 1 (29 mmol) was dissolved in 50 ml of ethanol and 30 ml of cyclohexene, and 200 mg of 10 % palladium on carbon added under nitrogen with magnetic stirring. After heating at reflux for 5 hr the mixture was filtered through infusorial earth, washing the earth
10 with ethanol. Concentration *in vacuo* of the filtrate gave 11.84 g of crude product. This was crystallized from 20 ml of ethyl acetate and 50 ml of hexanes to give 2.85 g of product (Compound I-30), mp 118-120 °C. HPLC/MS and NMR agreed with the assigned structure.

L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate) (Compound
15 I-3) was obtained in an analogous manner starting with 2-O,3-O-dibenzyl-L-ascorbic acid, 5-O,6-O-bis(2,2-dimethylpropionate).

Synthetic Preparation 3: 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid.

To an ice-cold solution of 5.21 g (14.6 mmol) of
20 2-O,3-O-dibenzyl-L-ascorbic acid in 35 ml of dry pyridine under nitrogen with magnetic stirring was added 2.26 g (19.0 mmol) of phenylisocyanate. After 20 hr at room temperature, it was concentrated *in vacuo* to give a mixture (HPLC/MS) of starting material, mono adducts, diphenylurea, and bis adduct. This was column chromatographed on a 5x26 cm silica gel column packed in hexanes and
25 gradient eluted from 5 to 50 % ethyl acetate. After 4 liters of elutant (around 30 % ethyl acetate) about 4 g of material that was 80 % desired, 15 % diphenylurea, and 5 % of bis adduct were obtained. Recrystallization from methanol multiple times gave 2.04 g of material which was > 95 % of the desired 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid by HPLC/MS and
30 NMR.

Synthetic Preparation 4: 6-O-phenylaminocarbonyl-L-ascorbic acid
(Compound I-21).

A solution of 2.04 g of the material obtained in Synthetic Preparation 3 in 4 ml of cyclohexene and 6.5 ml of ethanol was heated to reflux
5 under nitrogen with magnetic stirring with 130 mg of 10 % palladium on carbon for 1.3 hr. After filtration through infusorial earth and washing with ethanol, the filtrate was concentrated *in vacuo*. Separately, a 1.47 g sample of 2-O,3-O-dibenzyl-6-O-phenylaminocarbonyl-L-ascorbic acid which also contained about 25 % diphenylurea was treated in the same manner. After
10 filtration and concentration it was dissolved in ethyl acetate, extracted into 9 ml of 1M sodium hydroxide solution, acidified with 10 ml of 1M hydrochloric acid solution, ethyl acetate extracted 3 times, dried over sodium sulfate, filtered, and concentrated *in vacuo* to give 1.23 g of oil. The materials were combined and recrystallized from ethyl acetate/hexanes to give 1.87 g 6-O-phenylamino-
15 carbonyl-L-ascorbic acid (Compound I-21), mp 171 – 172°C with bubbling and decomposition. The structure was confirmed by HPLC/MS and NMR.

Example 1 – Preparation of Aqueous-Based Photothermographic Materials:

Aqueous-based photothermographic materials of this invention
20 were prepared in the following manner.

Preparation of Silver Benzotriazole Dispersion:

Solution A was prepared in a stirred reaction vessel by dissolving 85 g of lime-processed gelatin and 25 g of phthalated gelatin in 2000 g of deionized water.
25 Solution B containing 185 g of benzotriazole, 1405 g of deionized water, and 680 g of a 2.5 molar solution of sodium hydroxide was prepared. The mixture in the reaction vessel was adjusted to a pAg of 7.25 and a pH of 8.0 by addition of 2.5 molar sodium hydroxide solution as needed, and maintaining it at temperature of 36°C.
30 Solution C containing 228.5 g of silver nitrate and 1222 g of deionized water was added to the reaction vessel at an accelerated flow rate

defined by: $\text{Flow} = 16(1 + 0.002t^2)$ ml/min (where t is the time in minutes), and the pAg was maintained at 7.25 by simultaneous addition of Solution B. This process was terminated when Solution C was exhausted, at which point Solution D containing 80 g of phthalated gelatin and 700 g of deionized water at 40°C was added to the reaction vessel. The mixture was then stirred and the pH was adjusted to 2.5 with 2 molar sulfuric acid to coagulate the silver salt emulsion. The coagulum was washed twice with 5 liters of deionized water, and redispersed by adjusting pH to 6.0 and pAg to 7.0 with 2.5 molar sodium hydroxide solution and Solution B. The resulting dispersion contained fine particles of silver benzotriazole.

Preparation of Tabular Grain Silver Halide Emulsions:

A reaction vessel equipped with a stirrer was charged with 6 liters of water containing 4.21 g of lime-processed bone gelatin, 4.63 g of sodium bromide, 37.65 mg of potassium iodide, an antifoamant, and 1.25 ml of 0.1 molar sulfuric acid. The solution was held at 39°C for 5 minutes. Simultaneous additions were then made of 5.96 ml of 2.5378 molar silver nitrate and 5.96 ml of 2.5 molar sodium bromide over 4 seconds. Following nucleation, 0.745 ml of a 4.69% solution of sodium hypochlorite was added. The temperature was increased to 54°C over 9 minutes. After a 5-minute hold, 100 g of oxidized methionine lime-processed bone gelatin in 1.412 liters of water containing additional antifoamant at 54°C were then added to the reactor. The reactor temperature was held for 7 minutes, after which 106 ml of a 5 molar sodium chloride solution containing 2.103 g of sodium thiocyanate was added. The reaction was continued for 1 minute.

During the next 38 minutes, the first growth stage took place wherein solutions of 0.6 molar AgNO_3 , 0.6 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal uniform iodide level of 4.2 mole %. The flow rates during this growth segment were increased from 9 to 42 ml/min (silver nitrate) and from 0.8 to 3.7 ml/min (silver iodide). The flow rates of the sodium bromide were allowed to

fluctuate as needed to maintain a constant pBr. At the end of this growth segment 78.8 ml of 3.0 molar sodium bromide were added and held for 3.6 minutes.

During the next 75 minutes the second growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a
5 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were increased from 8.6 to 30 ml/min (silver nitrate) and from 4.5 to 15.6 ml/min (silver iodide). The flow rates of the sodium bromide were allowed to fluctuate as needed to maintain a constant pBr.

10 During the next 15.8 minutes, the third growth stage took place wherein solutions of 3.5 molar silver nitrate, 4.0 molar sodium bromide, and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a nominal iodide level of 4.2 mole %. The flow rates during this segment were 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The temperature was
15 decreased to 47.8°C during this segment.

During the next 32.9 minutes, the fourth growth stage took place wherein solutions of 3.5 molar silver nitrate and 4.0 molar sodium bromide and a 0.29 molar suspension of silver iodide (Lippmann) were added to maintain a
20 nominal iodide level of 4.2 mole %. The flow rates during this segment were held constant at 35 ml/min (silver nitrate) and 15.6 ml/min (silver iodide). The temperature was decreased to 35°C during this segment.

A total of 12 moles of silver iodobromide (4.2% bulk iodide) were formed. The resulting emulsion was coagulated using 430.7 g of phthalated lime-processed bone gelatin and washed with de-ionized water. Lime-processed bone
25 gelatin (269.3 g) was added along with a biocide and pH and pBr were adjusted to 6 and 2.5 respectively.

The resulting emulsion was examined by Scanning Electron Microscopy. Tabular grains accounted for greater than 99% of the total projected area. The mean ECD of the grains was 2.369 μm . The mean tabular thickness
30 was 0.062 μm .

This emulsion was spectrally sensitized with 1.0 mmol of blue sensitizing dye SSD-1 per mole of silver halide. Chemical sensitization was carried out using 0.0055 mmol of sulfur sensitizer (compound SS-1a) per mole of silver halide at 60°C for 10 minutes.

5 Preparation of Photothermographic Materials:

Solution A: Silver benzotriazole and gelatin (35% gelatin/65% water) were placed in a beaker and heated to 50°C for 15 minutes to melt the material. A 5% aqueous solution of 3-methylbenzothiazolium iodide was added. Mixing for 15 minutes was followed by cooling to 40°C. The sodium salt of
10 benzotriazole was added and the mixture was stirred for 15 minutes. Compound T-1 was then added. Mixing for 15 minutes was followed by addition of 2.5 N sulfuric acid to adjust the pH to 5.5. ZONYL[®] FSN surfactant was then added.

Solution B: A portion of the tabular-grain silver halide emulsion prepared above was placed in a beaker and melted at 40°C.

15 Solution C: Solution C was prepared by adding the dry materials to water and heating to 40°C.

Solution D: Solution D was prepared by adding the dry materials to water and heating to 55°C. The finished solution was allowed to cool to 40°C before use.

20 Solutions A, B, and C were mixed immediately before coating to form a photothermographic emulsion formulation. Solutions A, B, and D were mixed immediately before coating to form a photothermographic emulsion formulation. Each formulation was coated as a single layer on a 7 mil (178 µm) transparent, blue-tinted poly(ethylene terephthalate) film support using a knife
25 coater to form an imaging layer having the dry composition shown in the following TABLE II. Samples were dried at 120°F (48.9°C) for 7 minutes. Control sample (Sample 1-1-C) contained ascorbic acid while the inventive example (Sample 1-2) had Compound I-1 as the developer. The inventive developer, Compound I-1, was added in an equivalent molar amount to that of
30 ascorbic acid used in control sample 1-1-C.

TABLE II

Solution	Component	Dry Coating Weight (g/m ²)
A	Silver (from Ag benzotriazole salt)	1.82
A	Lime processed gelatin	1.10
A	3-Methylbenzothiazolium Iodide	0.09
A	Sodium benzotriazole	0.10
A	Mercaptotriazole compound T-1	0.07
A	ZONYL [®] FSN surfactant	0.06
B	Silver (from AgBrI emulsion)	0.38
C	Succinimide	0.13
C	Dimethylurea	0.16
C	Compound A-1	0.06
C	Compound VS-1	0.09
C	Ascorbic Acid	2.10
D	Succinimide	0.13
D	Dimethylurea	0.16
D	Compound A-1	0.06
D	Compound VS-1	0.09
D	Compound I-1 (TABLE I)	3.15

Evaluation of Photothermographic Materials:

- 5 The resulting photothermographic films were imagewise exposed for 10⁻² seconds using an EG&G flash sensitometer equipped with a P-16 filter and a 0.7 neutral density filter. Following exposure, the films were developed by heating on a heated drum for 18 seconds at 150°C to generate continuous tone wedges. These samples provided initial D_{min}, D_{max}, and Relative Speed.

The speeds are reported as "relative speed." "Relative Speed-2" was determined at a density value of 1.00 above D_{min} . Speed values were normalized. Sample 1-1, which contained ascorbic acid, was assigned a relative speed value of 100.

5 Densitometry measurements were made on a custom built computer-scanned densitometer and meeting ISO Standards 5-2 and 5-3 and are believed to be comparable to measurements from commercially available densitometers. Density of the wedges was then measured with a computer densitometer using a filter appropriate to the sensitivity of the photothermographic
10 material to obtain graphs of density versus log exposure (that is, $D \log E$ curves). D_{min} is the density of the non-exposed areas after development and it is the average of the eight lowest density values.

Post-processing light stability was evaluated using two test procedures. The first test was performed on a Picker light box, where the
15 developed samples were subjected to 600 foot-candles of light (6456 lux) and a temperature of 108°F (42.2°C) for 24 hours. The change in D_{min} (ΔD_{min}) was calculated by subtracting the initial D_{min} from the D_{min} after completion of the 24 hour test. The D_{min} values were read with an X-Rite, point densitometer. The results are tabulated in TABLE III below.

20 Developed samples were also evaluated for post-processing light stability. Samples were placed in a controlled environment at 70°F (21°C) and 50% RH (relative humidity) for 24 hours while being subjected to 100 foot-candles (1076 lux) of light. A metal bar was placed over a portion of each sample, and the protected portion was used as a reference region. The change in
25 D_{min} (ΔD_{min}) was calculated by subtracting the D_{min} of the reference region from the D_{min} of the sample that had been exposed for 24 hours. The D_{min} values were read with an X-Rite, point densitometer.

The results, shown below in TABLE III, record the initial sensitometry and post-processing light stability measurements. The reduction in
30 change of D_{min} (ΔD_{min}) demonstrates that the use of the specific ascorbic acid

derivatives as reducing agents according to this invention, provide photothermographic materials with improved post-processing light stability.

TABLE III

Sample	Reducing Agent	Dmin	Dmax	Relative Speed-2	Light Box Test (ΔD_{\min})	70/50 Test (ΔD_{\min})	Invention (I) or Comparison (C)
1-1-C	Ascorbic Acid	0.291	2.69	100	0.43	0.74	C
1-2	I-1	0.293	2.53	95	0.03	0.14	I

Example 2 Evaluation of Ascorbic Acid Derivatives:

A tabular-grain silver halide emulsion was prepared as described in Example 1. This emulsion was spectrally sensitized with 1.0 mmol of blue sensitizing dye SSD-1 per mole of silver halide. Chemical sensitization was
5 carried out using 0.0055 mmol of gold sensitizer (potassium tetrachloroaurate) per mole of silver halide and 0.0055 mmol of sulfur sensitizer (compound SS-1a) per mole of silver halide at 60°C for 10 minutes.

Preparation of a Photothermographic Emulsion Layer:

Solution B: A portion of the tabular-grain silver halide emulsion
10 was placed in a beaker and melted at 40°C.

Solution E: Silver benzotriazole and gelatin (35% gelatin/65% water), were placed in a beaker and heated to 50°C for 20 minutes to melt the material. A 5% aqueous solution of 3-methylbenzothiazolium iodide was added. Mixing for 15 minutes was followed by cooling to 40°C. The solution was
15 finished with the addition of ZONYL[®] FSN surfactant.

Solutions B and E were mixed immediately before coating to form a silver emulsion formulation. Multiple coatings of the identical silver emulsion formulation were prepared. Each equivalent formulation was coated as a single layer on a 7 mil (178 μ m) transparent, blue-tinted poly(ethylene terephthalate)
20 film support using a knife coater to form a layer having the dry composition shown in the following TABLE IV. Samples were dried at 120°F (48.9°C) for 7.5 minutes.

TABLE IV

Solution	Component	Dry Coating Weight (g/m ²)
B	Silver (from AgBrI emulsion)	0.38
E	Silver (from Ag benzotriazole salt)	1.82
E	Lime processed gelatin	1.10

E	3-Methylbenzothiazolium Iodide	0.09
E	ZONYL® FSN surfactant	0.06

Preparation of Developer Layer Incorporating Ascorbic Acid Derivatives:

Solution F: Solution F was prepared by adding the dry materials to methanol.

5 Solution G: Solution G was prepared by dissolving Vinol 523 in water with heating.

Solutions F and G were mixed with agitation resulting in a solution containing 50% methanol and 50% water. Benzotriazole and ascorbic acid compound (materials H in TABLE V below) were added as solids to the combined
10 solution and dissolved. The ascorbic acid derivative reducing agents described for this invention and ascorbic acid (comparison), were added at the same molar equivalent.

Each solution was coated on top of a sample of the previously coated silver lower layer prepared above. The coating was performed using a
15 knife coater to form a layer having the dry composition shown in the following TABLE V. Samples were dried at 120°F (48.9°C) for 7.5 minutes.

TABLE V

Solution	Component	Dry Coating Weight (g/m ²)
F	Mercaptotriazole compound T-2	0.07
F	Compound VS-1	0.15
F	Succinimide	0.21
F	Dimethylurea	0.21
F	Compound A-1	0.09
G	Vinol 523	2.82

H	Benzotriazole	0.75
H	Reducing agent: Ascorbic acid or ascorbic acid derivative	0.017 mol/m ²

Evaluation of Photothermographic Materials:

The resulting photothermographic materials were imagewise exposed and developed as described in Example 1. Developed samples were evaluated for post-processing light stability after being placed in a controlled environment at 70°F (21°C) and 50% RH (relative humidity) for 24 hours while being subjected to 100 foot-candles of light (1076 lux) as described in Example 1.

The changes in the minimum density (ΔD_{\min}), shown below in TABLE VI, demonstrate that compounds of this invention helped reduce the ΔD_{\min} over time and provide increased print stability.

TABLE VI

Example	Reducing Agent	ΔD_{\min}
2-1-C	L-Ascorbic Acid (Comparison)	0.61
2-2	I-1 (TABLE I)	0.17
2-3	I-3 (TABLE I)	0.08
2-4	I-5 (TABLE I)	0.21
2-5	I-6 (TABLE I)	0.41
2-6	I-7 (TABLE I)	0.12
2-7	I-8 (TABLE I)	0.02
2-8	I-9 (TABLE I)	0.05
2-9	I-10 (TABLE I)	0.12
2-10	I-12 (TABLE I)	0.15
2-11	I-13 (TABLE I)	0.17
2-12	I-14 (TABLE I)	0.17

2-13	I-15 (TABLE I)	0.37
2-14	I-16 (TABLE I)	0.38
2-15	I-17 (TABLE I)	0.47
2-16	I-18 (TABLE I)	0.35
2-17	I-27 (TABLE I)	0.09
2-18	I-28 (TABLE I)	0.09
2-19	I-29 (TABLE I)	0.03
2-20	I-30 (TABLE I)	0.22
2-21	I-31 (TABLE I)	0.34

Example 3:

The following example demonstrates that ascorbic acid compounds
5 within the scope of the present invention can be used as reducing agents in thermographic materials.

A 20 cm x 1 cm strip of thermographic material was prepared using the materials described in Example 1 but without photosensitive silver bromoiodide emulsion (Solution B). The strip was heated on a Reichert Heizbank
10 heating block system (Kofler Reichert, Austria) with a temperature gradient from 68°C to 212°C for 15 seconds. Densitometry measurements were carried out on an X-Rite® Model 301 densitometer. A development onset temperature of 175°C was found. A D_{max} optical density of 3.9 was obtained. The D_{min} optical density remained at 0.18 at temperatures below 110°C.

15 Thus, thermographic materials containing the ascorbic acid derivatives within the present invention are capable of providing images with excellent D_{min} and D_{max}.

The invention has been described in detail with particular reference
20 to certain preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.